

## PHOTOCATALYTIC PARTICLES IN FLOOR LAMINATES

### Field of the invention

The present invention relates to improved floor covering. In an embodiment, the present invention relates to floor covering formed of laminated panels. In another embodiment the present invention relates to carpet floor covering. In particular it relates to floor covering such as floor laminates or carpets comprising photocatalytic particles having many functions of antimicrobial, preventing smell or stainproof, or decomposition of harmful substances (NO<sub>x</sub>, and the like) based on the photocatalytic function.

### Background of the invention

- 5 The present invention relates to improved floor covering. In an embodiment, the present invention relates to floor covering formed of laminated panels. In another embodiment the present invention relates to carpet floor covering. In particular it relates to floor covering such as floor laminates or carpets comprising photocatalytic particles having many functions of antimicrobial, preventing smell or stainproof, or decomposition of harmful substances (NO<sub>x</sub>, and the like) based on the photocatalytic function.
- 10 For many decades, carpets and laminates have been the floor coverings of choice for improving both the aesthetics and comfort in residential homes and commercial buildings. Decorative laminates and carpet are well known and used for instance as covering material on walls, cupboard doors and desks, on tables and other furniture and as flooring material.
- 15 The laminates are often made of a base of particle board or fiber board provided with a monochromatic or patterned decor sheet impregnated with melamine-formaldehyde resin and a fine so-called overlay sheet of a-cellulose impregnated with melamine-formaldehyde resin. These sheets can be laminated to the base under heat and pressure. The overlay sheet is intended to protect the decor sheet from abrasion. In certain cases
- 20 the overlay sheet is omitted.

Since long the industry of laminated flooring tries to enhance the technical properties of laminated flooring. In the past the main focus has been laid on the technical performance of the product such as better carrier boards, lower expansion coefficient, click system, better durability and abrasion resistance of the surface. The decorative layer can be

- 25 protected by either an overlay of paper saturated with melamine resins and a certain content of AlO<sub>2</sub> to make the product abrasive resistant, or by saturation of the decorative printed paper with a suspension of melamine urea formaldehyde resins and a certain amount of aluminum oxide. Another method to treat and protect the decorative layer is the application of lacquers and hardening with electron beam curing.
- 30 Though very pleasing in appearance and convenience when new, carpets and floor laminates still have several disadvantages such as for example the continuous release of harmful substances. In addition floor coverings are susceptible to staining by foods and beverages and also discoloration due to soil pick-up caused by foot traffic. Moreover, floor

coverings are usually strongly glued by synthetic adhesives. Synthetic adhesive having fungus resistance performance are often used. Air pollution is an issue that has been discussed for many years. Pollutants in the air have been proved to affect human comfort and health. Relatively recently, it has been found that the quality of the air inside a home or business is frequently worse than the quality of the air outside that very same home or business. There are many cases where building residents complain of symptoms such as irritation of eye and nose, headache, tiredness and drying of throat and skin, as a result of the floor covering employed. The problem has been termed the Sick Building syndrome, and it has been proved that many of the symptoms of this syndrome are caused by volatile organic compounds (hereafter VOC) in the ambient air within the building. It is considered that the main cause is solvents used for adjustment of synthetic adhesives, for example, formaldehyde (it is also a carcinogen) derived from formalin.

In addition, surface treatments are often used in order to protect the floor coverings and/or to polish them. As the surface treatment, synthetic resin, for example, acryl resin emulsified polishing agent and a product filled in a synthetic resin bottle with a nozzle for spray is generally used. However these polishing agents often contain solvents harmful for human body. In addition, living spaces of residences and offices may carry airborne malodorous substances including sulfur compounds such as hydrogen sulfide and methyl mercaptan, nitrogen compounds such as ammonia, and other compounds such as fatty acid. To provide a comfort of living environment, it is desirable to treat the contaminated air for removal of the malodorous substances.

It is an object of the present invention to provide an improved floor covering wherein the volatilization or release of organic solvents is reduced. It is another object of the present invention to provide an improved floor covering having fungus resistance and bacterial resistance properties. It is yet a further object of the present invention to provide a floor covering having deodorizing and stainproofing properties.

#### **Summary of the invention**

In a first aspect, the present invention provides laminates comprising a decorative upper layer, optionally a protective overlay and optionally a base layer, wherein said decorative upper layer comprises a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder.

The present invention also provides laminates comprising a decorative upper layer, a protective overlay and optionally a base layer, wherein said protective overlay comprises

a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder.

The present invention encompasses decorative layers for laminate comprising a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a

5 binder.

The present invention also encompasses protective overlays, wherein said protective overlay comprises a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder.

The present invention also provides a process for the production of a decorative layer or a

10 protective overlay according to the present invention, comprising the step of providing a fiber web layer, treating said fiber web layer with a photocatalyst composition comprising photocatalyst particles, a binder and a solvent, and hardening said treated fiber web to obtain a decorative layer or a protective overlay comprising a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder.

15 The present invention provides the advantage that the laminates, the decorative layer and the overlay according to the present invention are excellent in the points that they show a deodorant function, an antimicrobial function or an antistain function due to photocatalyst particles comprised in said laminates.

20 The laminates of the present invention have the advantages of being anti staining, selfcleaning, antimicrobial and desodorizing. The photocatalyst particles comprised in said laminates will actively decompose toxic and non-biodegradable pollutants. Said photocatalysts will also mineralize any organic pollutants into CO<sub>2</sub>, H<sub>2</sub>O and inorganic compounds. These reactions can be activated by the sunlight, and when said photocatalysts are tuned by visible light.

25 In a second aspect, the present invention further provides carpet having air clarifying properties which has undergone a post-treatment with a finishing composition comprising the photocatalyst composition described above, optionally in combination with stain blockers such as grease and water stain fluoride-based repellent.

30 The present invention also provides a finishing composition comprising (a) a photocatalyst composition as defined herein, (b) a liquid carrier and (c) optionally a coacervate, wherein said photocatalyst composition comprises (i) photocatalyst particles, (ii) a binder and (iii) a solvent. In an embodiment, said photocatalyst particles are selected from the group comprising TiO<sub>2</sub>, ZnO, SiO<sub>3</sub>; Ti<sub>1-x</sub>Sn<sub>x</sub>O<sub>2</sub>, SrTiO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CdS, CdSe, WO<sub>3</sub>, FeTiO<sub>3</sub>, GaP,

GaAs, GeAs, RuO<sub>2</sub>, MoS<sub>3</sub>, LaRhO<sub>3</sub>, CdFeO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, MoS<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, CdO, SnO<sub>2</sub>, SiC, InP and/or mixture thereof. Preferably said photocatalyst particle is anatase TiO<sub>2</sub>.

The present invention also encompasses the use of a finishing composition according to the invention, for the treatment of carpets. The present invention further encompasses a

5 Method for the preparation of a carpet having air clarifying properties comprising the steps of: providing a finishing composition according to the invention, and applying said finishing composition onto a carpet thereby obtaining a carpet having air clarifying properties.

The present invention also encompasses carpet having air clarifying properties obtained by a method according to the invention.

10 The object of the present invention is to provide a photocatalytic process for treating an indoor environment contaminated by bacteria and airborne particulate or volatile substances which may be carried out without resort to a light source which is harmful to human being.

15 The laminates, overlay, decorative layers or carpets having air clarifying properties according to the invention do not necessitate the use of a special light source for excitation of the photocatalyst particles. They permit to photocatalytically treat an indoor environment or air. When bacteria and/or airborne substances are brought in contact with the photocatalyst particles comprised in said laminates, they are photodecomposed in situ.

20 **Brief description of Figures**

**Figure 1** illustrates the experimental arrangement for the assessment of degradation of volatile organic compound (VOC) by the floor covering according to the invention.

25 **Figure 2** illustrates the results of an experiment measuring the catalytic activity of TiO<sub>2</sub> coated carpet by the analysis of the effect of the coated carpets on formaldehyde degradation under continuous aeration.

**Figure 3** illustrates the results of an experiment measuring the catalytic activity of TiO<sub>2</sub> coated carpet by the analysis of the effect of the coated carpets on benzene degradation under continuous aeration.

30 **Figure 4** illustrates the results of olfactory evaluation of the tobacco odor deodorant property of the carpets according to the invention.

**Figure 5** illustrates the results of olfactory evaluation of the tobacco odor deodorant property of the carpets according to the invention.

**Figure 6** illustrates determination of the catalytic degradation of total volatile organic compound (TVOC) by the carpets according to the invention under continuous aeration.

**Figure 7** illustrates the results of an experiment measuring the effect of the duration of UV light illumination on the catalytic formaldehyde degradation property of the carpets according to the invention under continuous aeration.

**Figure 8** illustrates the results of an experiment determining the air cleaning durability of a carpet according to the invention under conditions intended to simulate a 5 year cycle of maintenance.

**Figure 9** illustrates determination of the catalytic formaldehyde degradation property of the laminates according to the invention.

**Figure 10** illustrates determination of the catalytic benzene degradation property of the laminates according to the invention.

#### **Detailed description**

The present invention relates to floor covering exhibiting catalytic properties to reduce

VOC-level in the indoor air.

As used herein, "a" includes both the singular and plural.

The recitation of numerical ranges by endpoints includes all numbers and fractions subsumed within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5).

The present invention provides solutions to indoor air problems by providing floor covering

having air clarifying, anti staining, self-cleaning, antimicrobial and deodorizing properties.

As used herein the term "air clarifying properties" means that the substrate showing such properties can remove unpleasant odors, and/or removes and decompose harmful substances and contaminants in the air.

In a first aspect, the present invention relates in particular to laminates comprising a

decorative upper layer, optionally a protective overlay and optionally a base layer, characterized in that the decorative upper layer comprises a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder. In another embodiment, the laminates according to the invention comprise a decorative upper layer, a protective overlay and optionally a base layer, characterized in that said protective

overlay comprises a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder.

The term "a protective overlay" as used herein refers to one or more overlay.

The term particle is to be understood in a very broad sense, including powders, dusts, fine granulates, filings and fibers, i.e. all forms of particles able to be distributed over a surface in a largely even manner.

5 The overlay and the decorative layer according to the present invention comprise a fiber web made of any suitable fiber. In an embodiment of the present invention said fibers are cellulose fibers. However, other materials, either on the basis of cellulose or not, are not excluded. Preferably said overlay and the decorative layer are made of thin sheet of paper.

10 As an example of the photocatalyst particles, which may be deposited into and/or onto these laminates, overlays or decorative papers, there may be mentioned oxide and non-oxide semiconductors such as  $TiO_2$ ,  $ZnO$ ,  $SiO_3$ ;  $Ti_{1-x}Sn_xO_2$ ,  $SrTiO_3$ ,  $Fe_2O_3$ ,  $CdS$ ,  $CdSe$ ,  $WO_3$ ,  $FeTiO_3$ ,  $GaP$ ,  $GaAs$ ,  $GeAs$ ,  $RuO_2$ ,  $MoS_3$ ,  $LaRhO_3$ ,  $CdFeO_3$ ,  $Bi_2O_3$ ,  $MoS_2$ ,  $In_2O_3$ ,  $CdO$ ,  $SnO_2$ ,  $SiC$ ,  $InP$  and/or mixture thereof. In a preferred embodiment  $TiO_2$ ,  $ZnO$ ,  $SiO_3$ ;  $CdS$ ,  $CdSe$ ,  $GaP$ ,  $MoS_3$ ,  $SiC$ , and the like are used. In an embodiment they are used on a 15 nanoscale size. They are excellent in the points that they show a deodorant function, an antimicrobial function or an antistain function due to decomposition of an organic compound by oxidation. Among these,  $Fe_2O_3$ ,  $ZnO$ ,  $SnO_2$ , and the like are available in the point that starting materials are obtained cheaply, and further an anatase type  $TiO_2$  and  $SnO_2$  are more preferred in the point that fine particles having higher activity can be 20 easily obtained. Rutile form  $TiO_2$  metalized with copper, silver, platinum or other metals may also be used. The photocatalyst particles having photocatalytic function of the present application may be used either any one kind of these or in combination of two kinds or more by mixing.

25 Photocatalyst described herein are able to break down many organic pollutants totally or partially. In an embodiment of the present invention,  $TiO_2$  as anatase is preferred since high photocatalytic purification has been observed because of its strong oxidation power, high chemical durability and non-toxicity.  $TiO_2$  is an inorganic oxide, showing no absorption of any fraction of the visible light, thus it is not colored. In the region of shorter wavelength a strong absorption of UV radiation is observed. This is due to the promotion 30 of an electron out of the valence band into the conductive band. In its anatase modification the band gap is 3.05 eV. In its tuned form the band gap is 2.8 eV. In this process photo energy is transferred into chemical energy.

35 Without being bound by the theory it is believed that active oxygen species generated from the laminate according to the invention, act on a bad smell component or bacteria to show a deodorizing property or an antimicrobial property, and the like.

In an embodiment of the present invention, said photocatalyst particles may be doped or tuned by adding one or more element within the crystal lattice of said photocatalyst. In an embodiment of the present invention, said photocatalyst particles can be doped with elements selected from the group comprising Nb, Mo, Cr, V, Cu, Mg, Ag, Ru, Au, N, Nd, 5 Pd, Pt, Fe, Ni, Mn and the like. Said elements can be the atom as such or ion form of said atoms. They can be implanted from the surface to deep inside of the bulk of the photocatalyst in an amount of at least  $10^{15}$  ions per g of the photocatalyst. For example, incorporating specific metal ions into the titanium oxide catalysts allows the catalyst to absorb light not only in the ultraviolet region but also in the visible light regions of about 10 400 to 800 nm.

The present invention provides laminates comprising overlay layer or decorative layer having a web of fiber comprising photocatalyst particles embedded in a suitable binder. Non-limiting examples of suitable binder include melamine resin, urethane resin, celluloid, chitin, starch sheet, polyvinyl alcohol, polyester resins, urea-formaldehyde, 15 dicyandiamide-formaldehyde, epoxy resins, polyurethane resins, (poly)silane resins, (poly)siloxane resins, silazane resins, acrylamide resins, acrylic silicon resins, acrylurethane resins, polyacrylamide resins and the like and mixtures thereof.

The binders for use according to the invention may be modified so as to impart a hydrophobic and/or oleophobic surface properties to the laminate.

20 In another embodiment of the present invention, the laminate may comprises a decorative layer as used in the prior art and an overlay according to the invention. Said decorative layer for example, can be made of paper impregnated with resin, which can be imprinted with a variety of patterns, such as a wood pattern, a pattern in the form of stone, cork, or similar or even with a fancy pattern.

25 It is clear that still other layers can be provided to the laminate, such as an intermediate layer upon which the decorative layer is provided.

The base layer of the laminate of the present invention may be selected from the group comprising of fiber board, particle board, a plastic sheet, wood and the like. Said base layer may be made of finely-ground wood which preferably is glued, more particularly, 30 watertight glued. Still more particularly, said base can be made of HDF board (High Density Fiberboard) or MDF (Medium Density Fiberboard). In a preferred embodiment, said base layer is MDF.

Preferably, also a backing layer, also referred as balancing sheet or counteracting layer, can be applied at the underside of the base layer forming a counterbalancing element for

the top layers and, thus, guaranteeing the stability of the form of the floor laminate. This balancing sheet may consist of a material, for example paper, impregnated with a resin, for example, a melamine resin.

It was surprisingly found that the laminates according to the invention exhibit anti staining, 5 selfcleaning, antimicrobial and deodorizing properties. These laminates have a surface profile with improved properties over the current art.

The present invention further relates to decorative layers as described above. In a preferred embodiment, said decorative layer is made of cellulose fibers, such as paper. According to the present invention, said decorative layer is impregnated with a 10 composition comprising photocatalyst particles and a binder. Examples of suitable photocatalysts have been described herein. Preferably said decorative layer comprises on or in its fiber web  $TiO_2$  particles, and more preferably anatase  $TiO_2$ . As previously cited the photocatalyst particles used in said decorative layer may be doped with elements as described above. Suitable binders embedding said particles are the same as that 15 described above.

The decorative layers according to the invention according to the present invention can be used for manufacture and decoration of laminates, furniture components, flooring laminates and other surfaces where decoration is needed.

The present invention also relates to protective overlay comprised of a fiber web having 20 deposited thereon or therein photocatalyst particles embedded in a binder. Suitable binders embedding said particles are the same as that described above. Suitable photocatalyst particles comprised in said overlay are the same as that described above. Said photocatalyst may be additionally doped as described above. In a preferred embodiment, said overlay is provided with  $TiO_2$  particles and more in a particular with 25 anatase  $TiO_2$ .

In a preferred embodiment the protective overlay is made of one or more material layers such as cellulose fibers for example very thin layers of paper. Said overly may be a transparent or translucent, specially made cellulose paper into which additional abrasion-resistant particles can be woven, or which can be impregnated with any other abrasion-resistant particles, which give the laminate the desired resistance to wear and tear and the 30 hardness required for long-term use. Examples of suitable abrasion-resistant particles include but are not limited to mineral particles such as silica, alumina, alundun, corundum, emery, spinel, as well as other materials such as tungsten carbide, zirconium boride,

titanium nitride, tantalum carbide, beryllium carbide, silicon carbide, aluminum boride, boron carbide, diamond dust, and mixtures thereof.

The overlays according to the present invention can be used for manufacture of decorative laminates, furniture components, flooring laminates and other surfaces where 5 wear protection is needed.

In another aspect, the present invention also relates to a process for the manufacture of overlays and decorative layers and laminates according to the invention.

The decorative layer and the protective overlay according to the present invention, are prepared according to a process comprising the step of (a) providing a fiber web layer, (b) 10 treating said fiber web layer with a photocatalyst composition comprising photocatalytic particles, a binder and optionally at least one solvent, and (c) hardening said treated fiber web to obtain a decorative layer or a protective overlay comprising a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder.

Suitable photocatalyst particles used in the photocatalyst composition have been 15 described above and are selected from the group comprising  $TiO_2$ ,  $ZnO$ ,  $SiO_3$ ;  $Ti_{1-x}Sn_xO_2$ ,  $SrTiO_3$ ,  $Fe_2O_3$ ,  $CdS$ ,  $CdSe$ ,  $WO_3$ ,  $FeTiO_3$ ,  $GaP$ ,  $GaAs$ ,  $GeAs$ ,  $RuO_2$ ,  $MoS_3$ ,  $LaRhO_3$ ,  $CdFeO_3$ ,  $Bi_2O_3$ ,  $MoS_2$ ,  $In_2O_3$ ,  $CdO$ ,  $SnO_2$ ,  $SiC$ ,  $InP$  and/or mixture thereof. In a preferred 20 embodiment  $TiO_2$  is used on a nanoscale size. Although not limiting, when the composition comprises a suspension in a solvent, the photocatalyst may be employed in an amount ranging from 0.01 to 5 % by weight, for example in an amount ranging from 0.01 to 1% by weight and for example in an amount ranging from 0.05 to 0.3 %.

Examples of suitable binder have been described above and include but are not limited to 25 melamine resin, urethane resin, celluloid, chitin, starch sheet, polyvinyl alcohol, polyester resins, urea-formaldehyde, dicyandiamide-formaldehyde, epoxy resins, polyurethane resins, (poly)silane resins, (poly)siloxane resins, silazane resins, acrylamides resins, acrylic silicon resins, acrylurethane resins, polyacrylamide resins and the like and mixtures thereof. Although not limiting, when the composition comprises a suspension in a solvent, the binder may be employed in an amount ranging from 0.01 to 5 % by weight, for example in an amount ranging from 0.01 to 1% by weight and for example in an amount 30 ranging from 0.05 to 0.3 %.

In a preferred embodiment said photocatalyst composition comprises a solvent. Suitable solvents can be selected from the group comprising water, ethylene glycol butyl ether, aliphatic linear, branched or cyclic or mixed aromatic-aliphatic alcohols having 4 to 20 carbon atoms, such as methanol, ethanol, butanol, 2-propanol, isobutanol, isopropanol.

benzyl alcohol, methoxypropanol or furfuryl alcohol; and the like, and/or mixture thereof. In an embodiment, said solvent is selected from the group comprising water, ethylene glycol butyl ether, ethanol and the like, and/or mixture thereof. In a preferred embodiment said solvent is water. The photocatalyst composition may further comprise additional solvent 5 such as for example ethylene glycol butyl ether. In a preferred embodiment, said photocatalyst composition is a suspension comprising the photocatalyst particles, a binder and at least one solvent. Although not limiting, the solvent can be employed individually or as a mixture, and in particular in a amount ranging from 50 to 99 % by weight, for example in an amount ranging from 80 to 99% by weight and for example in an amount ranging 10 from 90 to 99 %.

In another embodiment, the photocatalyst particles can be dispersed or otherwise introduced into a molten, uncrosslinked, uncured or dissolved form of a suitable binder.

The photocatalyst composition for use in the present invention may further comprise antimicrobial agents. Although not limiting, up to 1 % by weight of antimicrobial agents 15 may be added to the photocatalyst composition.

Antimicrobial agents suitable for said photocatalyst composition may be any chemical capable of preventing the growth of or killing microorganisms. Examples of suitable antimicrobial agents include, but are not limited to, quaternary ammonium, phenolic, amide, acid, and nitro compounds, and mixtures thereof. Examples of suitable quaternary 20 ammonium compounds include, but are not limited to, 2-(3-anilinovinyl)3,4-dimethyl-oxazolinium iodide, alkylisoquinolium bromide, benzalkonium chloride, benzethonium chloride, cetylpyridinium chloride, chlorhexidine gluconate, chlorhexidine hydrochloride, lauryl trimethyl ammonium compounds, methylbenzethonium chloride, stearyltrimethyl ammonium chloride, and mixtures thereof. Examples of suitable phenolic compounds 25 include, but are not limited to, benzyl alcohol, p-chlorophenol, chlorocresol, chloroxylenol, cresol, o-cymene-ol (BIOSOL), hexachlorophene, hinokitiol, isopropylmethylphenol, parabens (having methyl, ethyl, propyl, butyl, isobutyl, isopropyl, and/or sodium methyl substituents), phenethyl alcohol, phenol, phenoxyethanol, o-phenylphenol, resorcin, resorcin monoacetate, sodium parabens, sodium phenolsulfonate, thioxolone, 2,4,4'-trichloro hydroxidiphenyl ether, zinc phenolsulfonate, di-tert.-butyl phenole, hydrochinone, and mixtures thereof. Examples of suitable amides include, but are not limited to, diazolidinyl urea, 2,4-imidazolidinedione (HYDATOIN), 3,4,4'-trichlorocarbanilide, 3-trifluoromethyl-4,41-dichlorocarbanilide, undecylenic acid monoethanolamide, and mixtures thereof, more preferably still 2,4-imidazolidinedione. Examples of suitable acids 30 include, but are not limited to, ascorbic acid, benzoate, benzoic acid, citric acid, 35

dehydroacetic acid, potassium sorbate, salicylic acid derivatives such as acetyl salicylic acid, salicylic acid aldehyde, sodium citrate, sodium dehydroacetate, sodium salicylate, sodium salicylic acid, sorbic acid, undecylenic acid, zinc undecylenate, and mixtures thereof. Examples of suitable nitro compounds include, but are not limited to, 2-bromo 5 nitro-2,3-propanediol (BRONOPOL), and methyldibromo glutaronitrile and propylene glycol (MERGUARD), and mixtures thereof. In a preferred embodiment said antimicrobial agent is hinokitiol.

The photocatalyst composition according to the present invention may further comprise abrasion-resistant particles. Examples of suitable abrasion-resistant particles include but 10 are not limited to mineral particle such as silica, alumina, alundun, corundum, emery, spinel, as well as other materials such as tungsten carbide, zirconium boride, titanium nitride, tantalum carbide, beryllium carbide, silicon carbide, aluminum boride, boron carbide, diamond dust, and mixtures thereof. Considering cost availability, hardness, particle size availability and lack of color, aluminum oxide is the preferred particles.

15 The photocatalyst composition according to the present invention may also contain auxiliaries or additives such as absorbents, rheological modifiers, plasticizers, antifoaming agents, antifouling agents, thixotropic agents, pigments, fillers, aggregates, extenders, reinforcing agents, flow control agents, catalysts, pigment pastes, mineral oils, wetting agents, adhesion promoters, thickening agents, flame-retarding agents, antioxidants, 20 elastomers, antisettling agents, diluents, UV light stabilizers, air release agents, solvents, dispersing aids, and mixtures thereof, additional hardeners and additional curable compounds, depending on the application.

For example the photocatalyst composition can be formulated as comprising 0.10 to 0.15 % by weight of photocatalyst particles, 0.10 to 0.20 % by weight of antimicrobial agent, 25 0.10 to 0.15% by weight of a binder, 0.03 to 0.05 % by weight of a solvent and above 98 % by weight of water. In a further example the photocatalyst composition can be formulated as comprising 0.10 to 0.15 % by weight of  $TiO_2$ , 0.10 to 0.20 % by weight of hinokitiol, 0.10 to 0.15% by weight of a binder, 0.03 to 0.05 % by weight of ethylene glycol butyl ether and above 98 % by weight of water.

30 Said treating step (b) is an impregnating step. In another embodiment said treating step (b) is selected from the group comprising dipping, flooding, coil coating, spraying, centrifuging, screen printing, vacuum infiltrating and the like.

The next step in the process according to the invention consists of the curing also referred as drying step (c).

The treated layer according to the invention is solidified, cured or otherwise hardened and processed to produce the overlay or decorative layer according to the invention. The term "cured" or "dried" as used herein is not limited to materials which are cross-linked, but is open to materials which set, harden or solidify by any known means such as 5 polymerization, heating, removal of solvent, freezing, chemical reaction, etc. The treated layer may be a decorative layer or an overlay.

In an embodiment said drying step may be performed by thermal hardening such as by heating, by infra red treatment, using laser and the like. Said heating may be performed for example using a metal plate, or a traditional oven and the like. Said drying step may 10 also be performed using radiation hardening such as UV, VIS, laser hardening, electron beam hardening and the like. When the drying step is a heating step the temperature may range from room temperature to 350 °C.

In accordance with the present invention, the photocatalyst composition for use herein is applied, coated or impregnated to the surface of a fibrous sheet using a suitable coating 15 device. The photocatalyst composition according to the invention can be applied to the sheet by any process used for applying a coating. Non-limiting examples of devices for depositing the photocatalyst composition according to the invention particles include a secondary headbox or a slot orifice coating head applicator. The term "slot orifice coater" as used herein is used in the same manner it is used in the art, namely, to designate a 20 coater having a central cavity which opens on and feeds a slot through which the coating is forced under pressure.

Except for the overlays and decorative layers according to the invention, the laminate of the present invention is suitably made according to standard practice and suitably has a conventional construction. The laminate is formed by superposing the different layers. 25 The final laminate is made in the typical way such as by stacking the different layers on a suitable press or pressing plate die and subjecting the assembly to sufficient heat and pressure between the bottom pressing plate die and a highly polished upper pressing plate die for a time sufficient to produce the desired decorative laminate. The conditions of pressing for both high pressure laminate and low-pressure laminate are standard and well 30 known.

Preferably, the laminates are realized according to the classical technique which is applied for forming DPL (Direct Pressure Laminate). It is evident that, according to a variant, the overlay and the decorative layer, already before their application on the base layer, may consist of a single layer.

After pressing, the laminate according to the present invention can be cut into individual panels. The laminates can be cut into floor panels of suitable sizes. These floor panels can be of various shape, for example, rectangular or square, or of any other shape. In an embodiment, they can be manufactured in an elongated form, with a length of for example 5 1 to 2 meters. The thickness can also vary. Although non-limiting, said thickness may range from 0.1 mm to 45 mm. Non limiting examples of suitable thickness range from 0.1 mm to 3 mm, from 5 to 15 mm, for example 8 mm. The panels can be provided on their side with suitable tongue and groove coupling. The groove and tongue profile is milled along the edges of the support, thereby allowing the individual panels to be joined up 10 during the laying process. The dimensions of the profiles are designed so that adjacent panels can be pushed or hit into each other.

The laminates or panels according to the invention can be treated at their sides with a surface densifying agent, more particularly a surface hardening agent, which preferably is chosen from the following series of products: impregnation agents, pore-sealing agents, 15 lacquers, resins, oils, paraffines and similar. This treatment can be performed over the complete surface of the sides or only over well-defined portions thereof, for example, exclusively the surfaces of the tongue and groove. The treatment with a surface densifying agent offers, in combination with the snap-together effect of the tongue and groove, the advantage that in various aspects better coupling features, are obtained. As a 20 result of this, the coupling parts better keep their shape and strength, even if the floor panels are engaged and disassembled repeatedly.

The floor laminates or panels according to the present invention can be applied in various ways. They can be attached at the underlying floor, either by gluing or by nailing them on. According to another possibility, the floor laminates may be installed loosely onto the 25 underground, whereby the floor laminates may mutually match into each other by means of a tongue and groove coupling, whereby mostly they are glued together in the tongue and groove, too. The floor obtained in this manner, also called a floating parquet flooring, has as an advantage that it is easy to install and that the complete floor surface can move which often is convenient in order to receive possible expansion and shrinkage 30 phenomena. The floor laminates may also be provided at the edges of two opposite sides, with coupling parts, co-operating with each other, substantially in the form of a tongue and a groove, whereby the coupling parts are provided with integrated mechanical locking means made in one piece with the panels which prevent the drifting apart of two coupled floor panels. The floor covering preferably is formed by joining the floor laminates into 35 each other free of glue. Hereby, the connections are of such nature that the floor panels

can be disassembled without being damaged, such that, for example, when moving, they can be taken along in order to be placed again. It is, however, clear that gluing between tongue and groove is not excluded.

The present invention provides laminates, and protective or decorative layer having

5 photocatalytic functions such as deodorant, antimicrobial activities and the like.

The invention is intended for so-called laminated floors, but generally it can also be applied for other kinds of floor covering, comprising hard floor panels, such as veneer parquet, prefabricated parquet, or other floor panels which can be compared to laminated floor. The invention is also suitable for carpets and mats such as car mats and the like.

10 In an embodiment of the present invention, said floor covering is a carpet which has undergone a post-treatment with a finishing composition comprising the photocatalyst composition described above, optionally in combination with stain resists such as grease and water stain fluoride-based repellent. As used herein the term "carpet" encompasses carpets, rug, mats and the like.

15 In an embodiment the finishing composition comprises (a) the photocatalyst composition as described above (b) a liquid carrier and optionally (c) a coarcervate. Said composition may further comprise soil resists products such as fluorocarbon to impart water and oil repellency. The finishing composition may also comprise a stain resists. The finishing composition may further comprise a softener for extra bulk.

20 In an embodiment of the invention, the finishing composition comprises the photocatalyst particles in an amount ranging from 0.01 to 5 % by weight of the photocatalytic composition, preferably from 0.01 to 1% by weight and most preferably from 0.05 to 0.3 % by weight.

25 In a further embodiment, the photocatalyst composition to be used in the finishing composition is added in a concentration comprised between 1 to 50 % by weight, preferably from 5 to 35 % by weight, more preferably from 7 to 20 % by weight, yet more preferably from 7 to 13 % by weight, most preferably from 8 to 9 %.

30 The liquid carrier is preferably an aqueous system. The carrier can also contain a low molecular weight organic solvent that is highly soluble in water, e.g., C1 to C4 monohydric alcohols, C2 to C6 polyhydric alcohols, such as alkylene glycols and polyalkylene glycols, alkylene carbonates, and mixtures thereof. Examples of these water-soluble solvents include ethanol, propanol and isopropanol. In an embodiment of the present invention the liquid carrier and the solvent to be used in the finishing composition and/or in the photocatalyst composition are each independently selected from the group comprising

water, alkylene glycols, polyalkylene glycols, alkylene carbonates, ethanol, propanol and isopropanol and mixtures thereof. Water is a preferred liquid carrier due to its low cost, availability, safety, and environmental compatibility. The water can be distilled, deionized, or tap water.

- 5 Highly preferred materials of this class of liquid carriers are those that do not cause any significant color change, nor impart any discoloration, such as graying or yellowing, to the carpets to which they are applied, either during treatment followed by drying and/or curing, or after the drying and/or curing step followed by normal exposure to the elements, such as air, moisture or sunlight exposure.
- 10 The level of liquid carrier to be used in the finishing composition can typically be from 50% to 99% of the composition, for example from 75% to 95%, and preferably from 80% to 90% of the composition, for example 87 to 89 %.

The coacervate for use in the finishing composition assists in solubilising the particles and provides a uniform film at the fiber surface. Said coacervate can be selected from the group comprising Levalin VKU-N (Bayer), Primasol SD (BASF), Irgapadol PN New (Ciba), Lyogen AF (Clariant AG), Intratex AF (Crompton & Knowles) and the like. The amount of coacervate to be used in the finishing composition can typically vary from 0 to 15 %, for example from 1 to 10 %, for example from 2 to 5 % and preferably from 2 to 4 %.

- 20 As described above for the photocatalyst composition, the binder to be used can be selected from the group comprising melamine resin, urethane resin, celluloid, chitin, starch sheet, polyvinyl alcohol, polyester resins, urea-formaldehyde, dicyandiamide-formaldehyde, epoxy resins, polyurethane resins, (poly)silane resins, (poly)siloxane resins, silazane resins, acrylamides resins, acrylic silicon resins, acrylurethane resins, polyacrylamide resins and the like and mixtures thereof. In an embodiment the binder is used in an amount ranging from 0.01 to 5 % by weight of the photocatalyst composition, preferably from 0.01 to 1% by weight, more preferably from 0.05 to 0.3 % by weight.
- 25

Suitable carpet fiber material which can be treated with the finishing composition are materials comprising for example, wool, polyamide, polyurethanes, polyester, polyacrylonitrile, polypropylene, polyethylene and cellulose-containing fiber materials of all kinds, for example natural cellulose fibers, such as cotton, linen, jute and hemp, and also regenerated cellulose. The materials may also be used as blends of natural fibers like cotton, wool or jute with each other or with synthetic fiber materials like PES, Nylon or polypropylene or blends of synthetic fiber materials with each other. Typical fiber blends

are of polyacrylonitrile-polyester, polyamide/polyester, polyester/cotton, polyester/viscose and polyester/wool.

A wide variety of stain resists and soil resists may be used in the finishing composition. Suitable stain resists are polymers containing phenol-formaldehyde, methacrylic acid, 5 maleic acid, sulfonated fatty acids, and blends of the above. Suitable soil resists are polymers containing fluorochemical residues with the most preferred being cationically dispersed. The use of cationic fluorochemicals in combination with anionic stain resists typically gives better fluorine retention. Suitable stain resists for the practice of this invention include, but are not limited to, phenol formaldehyde polymers or copolymers 10 such as CEASESTAIN and STAINAWAY (from American Emulsions Company, Inc., Dalton, Ga.), MESITOL (from Bayer Corporation, Pittsburgh, Pa.), ERIONAL (from Ciba Corporation, Greensboro, N.C.), TAMOL (from Rohm & Haas Co.), BAYPROTECT CL or CSD<sup>TM</sup> (from Bayer AG), INTRATEX (from Crompton & Knowles Colors, Inc., Charlotte, N.C.), NYLOFIXAN<sup>TM</sup> P (from Sandoz Corp.), ACRYSOL<sup>TM</sup> (from Rohm and Haas 15 Company) and CARBOPOL<sup>TM</sup> (from B. F. Goodrich), STAINKLEER (from Dyetech, Inc., Dalton, Ga.), LANOSTAIN (from Lenmar Chemical Corporation, Dalton, Ga.), and SR-300, SR-400, and SR-500 (from E. I. du Pont de Nemours and Company, Wilmington, Del.); polymers of methacrylic acid such as the SCOTCHGARD FX series carpet 20 protectors (from 3M Company, St. Paul, Minn.); LEUKOTAN<sup>TM</sup> family of materials such as Leukotan<sup>TM</sup> 970, Leukotan<sup>TM</sup> 1027, Leukotan<sup>TM</sup> 1028, and Leukotan<sup>TM</sup> QR 1083 (from Rohm and Haas Company), and sulfonated fatty acids from Rockland React-Rite, Inc., Rockmart, Ga.). Suitable soil resists for the practice of the present invention include, but are not limited to, fluorochemical emulsions such as AMGUARD (from American 25 Emulsions Company, Inc., Dalton, Ga.), SOFTECH (from Dyetech, Inc., Dalton, Ga.), LANAPOL (from Lenmar Chemical Corporation, Dalton, Ga.), SCOTCHGARD FC series carpet protectors (from 3M Company, St. Paul, Minn.), NK GUARD (from Nicca USA, Inc., Fountain Head, N.C.), UNIDYNE (from Diakin America, Inc., Decatur, Ala.), and ZONYL such as Zonyl 555, N-130 and N-119 (from E. I. du Pont de Nemours and Company, 30 Wilmington, Del.).

The amount of the stain resists and/or soils resists used in the preparations of the finishing composition of the present invention are the amounts typically employed in the carpet and fabric industry and would be well known to those skilled in the art. Ordinarily, depending upon the nature of the stain resist and/or soils resist and the carpet being treated and its location, the resists are applied to the material in an amount to result in a treatment rate of 0.1 wt % to 20 wt % based upon the weight of the carpet 35

being treated and the amount of stain resists and/or soils resists. Commonly, the treatment rate will be from 0.15 wt % to 10 wt %, preferably from 0.2 wt % to 4 wt %, more preferably from 0.25 wt % to 2 wt %. Most preferably, the stain resists and/or soils resists is applied to give a treat rate of 0.25 wt % to 1.0 wt % based upon the weight of the carpet  
5 being treated.

The finishing composition of the present invention may be provided with other active ingredients depending upon the application or surface to be treated. One such additional ingredient which may be utilized in the finishing composition depending upon the application is a foaming agent for producing a foam composition for treating the relatively  
10 absorbent surfaces of the carpet. Non-limiting suitable examples of foaming agents include lauryl sulphate, ammonium lauryl sulphate, sodium lauryl sulphate. The additional ingredients would be utilized in the compositions at the usually employed concentrations, generally 5 % by weight or less based upon the total weight of the finishing composition.

In an embodiment the finishing composition is prepared by emulsifying the photocatalyst  
15 composition in water, using equipment such as a sonicator, homogenizer, microfluidizer, high shear blending equipment and the like.

When treating or when preparing the carpets, to impart to said carpet air clarifying properties, the finishing composition may be applied to the surface at any stage during its manufacture. For example, when used to treat carpet, the finishing composition may be  
20 utilized to treat the precursor filaments, yarns or fibers prior to their use in the conventional manufacturing process. The filament or yarn may be run through a bath containing the finishing composition or the finishing composition may be sprayed on the filament. After the treatment, the filaments or yarns are dried and then further processed into carpet in the normal manner. Alternatively, the carpet during the manufacturing  
25 process may be immersed, sprayed or otherwise treated with the finishing composition. The carpet fibers may be sprayed or otherwise treated with the finishing composition prior to being inserted into the primary backing. Alternatively, the fibers may also be treated once they have been inserted into the primary backing, either before or after the backing adhesive and secondary backing material have been applied. The finishing composition  
30 may also be applied to the finished carpet as a final step prior to drying and rolling. The carpet would be sprayed or otherwise treated with the finishing composition, after which time the carpet would be dried in the usual manner and rolled onto the roll. The finishing composition can be applied to the carpet in an amount ranging from 10 g/m<sup>2</sup> to 100 g/m<sup>2</sup> of surface, for example from 20 g/m<sup>2</sup> to 70 g/m<sup>2</sup>, preferably from 40 g/m<sup>2</sup> to 60 g/m<sup>2</sup>, and  
35 preferably in an amount of 50 g/m<sup>2</sup>.

The finishing compositions according to the present invention can be applied to the carpets by a variety of methods. Examples of such methods include, but are not limited to, Beck dying procedures, continuous dyeing procedures, brushing, dipping, spraying, padding, roll-coating, foaming or the like. The finishing compositions can be applied to the carpet as such or in combination with other fluorofinishes, stainblockers, processing aids, 5 lubricants, anti-stains, etc. The compositions can also be blended with other agents that have oil/water repellency and soil release properties and applied to the carpets. They can be applied to dyed and undyed carpeting. In a preferred embodiment, the finishing composition is formulated as foam and can be roll-coated on the carpet. Once the 10 finishing composition applied the coated carpets exhibit fibers having uniform and even coating of photocatalyst particles of an average size of 2 µm with a spread of 0,5 to 4 µm.

In an embodiment of the invention, said finishing composition is provided as a foam. The finishing composition can then be applied by means of a foam applicator. Foam application has several advantages, it allows exact quantity controllable application and 15 an even application without any stripes. Low wet pick-up is observed and an adjustable penetration of the composition can be obtained. In addition this mode of application requires only little space. It is also ecologically beneficial and has a minimum impact on speed. The finishing composition can be applied after dyeing, before drying. In another embodiment the finishing composition can be applied during finishing. The finishing 20 composition can be applied as aqueous formulation in diluted, solubilised, emulsified or dispersed form.

Another option would be to apply the finishing composition to an installed carpet. When applying the finishing composition to an installed carpet, it is not essential, but preferred that the finishing composition be applied thoroughly and evenly throughout the length of 25 the pile, especially reaching down to the base of the pile fiber. This is generally achieved by applying an aqueous foaming finishing composition to the carpet and then working the fibers to improve the contact, distribution and penetration of the finishing composition. This is most commonly achieved by use of a pile brush operated either by hand or automatically for example, utilizing a cleaning device such as is commonly available 30 commercially. To enhance the penetration of the finishing composition, the fibers of the carpet may initially be wetted through an application of a detergent solution. This is most commonly applied where the installed carpet is cleaned using a cleaning machine prior to the application of the finishing composition. While the carpet fibers are still moist, the finishing composition may be applied and worked into the carpet, utilizing the pile brush. 35 Once the carpet has been so treated, it is dried, either by allowing it to dry in the air at

ambient temperature or through the use of hot air blown through the pile of the carpet to increase the speed of drying of the carpet. Depending upon the state of the carpet or other fibrous material, the finishing composition may be applied in many different ways. The composition may be applied by dipping the material in the finishing composition or by spraying the composition onto the fibrous material. In any of these cases, once the fiber or carpet is treated with the finishing composition, the treated carpet material is allowed to dry by way of applied heat or simply by ambient drying. Alternatively, or in addition to treating the carpet fiber with the finishing composition, the carpet backing and/or carpet cushion underlayment may also be treated with the finishing composition. Once again, the carpet backing and/or carpet cushion underlayment may be treated during the manufacturing process, or prior to its installation. The carpet cushion underlayment may also be similarly treated during the installation of the carpet cushion underlayment.

The present invention is in no way limited to the forms of embodiment described herein, on the contrary may such floor covering such as carpets, floor laminates, overlay and decorative layer, as well as said process, be realized in different variants without leaving the scope of the invention. The surprising properties of the floor covering according to the invention are shown in the present examples wherein the VOC degradation properties of the floor covering of the invention are illustrated. The following examples illustrate the use of the present invention but are not to be construed as limiting the scope of the present invention.

### Examples

In the following examples the VOC degradation properties of the floor covering according to the invention are determined. The tested VOC reference substances for indoor air were benzene, Formaldehyde (HCHO), TVOC (total volatile organic compound) and cigarette 25 smoke polluted indoor air (tobacco odor).

The experimental arrangement for the assessment of the VOC reducing properties of the floor covering according to the invention is shown in Figure 1. Briefly, the tested gas 4 flows out a container 15 comprising said gas in a concentrated form. The gas flows out of tube 6 through a regulation valve 8 into tube 9 which is connected to the test chamber 2. The concentrated gas is diluted and adjusted to the wanted concentration by means of pure air 6 flowing through tube 7 connected to the regulation valve 8. The air/gas mixture flows into tube 9 which is connected to the test chamber 2. The sample 1 to be analyzed is placed in the test chamber 2 which comprise a UV bulb 3. The gas flows out of the test chamber 2 through tube 10. A data logger 11 is connected to the arrangement and control 30 and/or measure the temperature, humidity and/or flow rate. The tested gas flowing out of

the test chamber 2 through tubing 10 is sampled through a valve 12 which is connected 17 to an olfactometer 13 and is also connected 16 to a sampling tube 4 for gas analysis.

**Example 1: Determination of the catalytic formaldehyde degradation property of the carpets according to the invention under continuous aeration**

5 In this example, the catalytic activity of TiO<sub>2</sub> coated carpet was measured by the analysis of the effect of the coated carpets on formaldehyde degradation under continuous aeration.

The carpet samples were made from 40 cm x 40 cm carpet pieces. From these carpet pieces, carpet samples of 7.8 cm x 7.8 cm were manufactured and masked by means of 10 an aluminum tape in order to avoid edge effects during the measurement of the catalytic degradation of the formaldehyde. Formaldehyde degradation was investigated under continuous aeration by chamber testing and compared with uncoated carpet samples, and with a control measurement performed in the test chamber without sample.

15 The test chambers are airtight aluminum boxes which have a volume of 49.58 l, the proportion between the tested sample and the chamber volume amounts to 1.23 m<sup>2</sup>/m<sup>3</sup> in a standard inspection surface of 61 cm<sup>2</sup>. The carpet samples were placed in the center of the test chambers and locked therein. A UV lamp of 80 W was fixed in the chamber on the top.

20 A defined formaldehyde concentration of 220 µg/m<sup>3</sup> +/- 30 µg/m<sup>3</sup> (which corresponds to the average formaldehyde content in a smoker room) was applied in the test chamber by means of a continuous air supply over a Teflon hose at an air exchange rate of 0.5/h. The test chambers were operated at a temperature of 20°C and a relative humidity of 50 %.

25 The formaldehyde originates from a 50 NI content high-grade steel container containing a concentrated formaldehyde atmosphere of 54000 µg/m<sup>3</sup>, in constant equilibrium between liquid and gaseous state at 20 °C and 50 % relative humidity. The formaldehyde flows out of this container at an air flow of 3.0 l/h (50 ml/min) and is mixed with pure air in ratio of 1:245. The air flows out of the test chambers at a flow rate of 180 l/h, wherein 24.8 l were sampled by means of diaphragm pumps.

30 The measurement of the formaldehyde concentrations were performed at the times t = 0, 2, 8 and 24 hours and after 2, 4, 7 and 14 days, so that altogether 8 samplings were performed by means of direct withdrawal from Septen with syringes.

In an additional control chamber without sample the appropriate measurements were made likewise at 0, 8, 24 hours as well as 7 and 14 days.

The laboratory tests were performed according to the respective DIN procedures and/or regulations wherein the aldehyde concentration was measured by use of the DNPH method (dinitrophenylhydrazine = DNPH). Subsequently, the samples were examined photometrically using pararosanilin procedure on formaldehyde.

5 The results of this experiment are shown in Figure 2.

The initial fluctuations in formaldehyde content observed in the test chamber are due mainly to errors due for examples to sampling point, time needed to adjust the concentration inside the test chamber and the like. This is verified by the measurements performed in the test chambers without samples. A clear difference between the samples  
10 according to the invention and the controls can be seen after 8 h.

It can be seen from Figure 2 that after few hours a clear decrease in the formaldehyde concentration was observed for the coated carpet samples wherein the concentration after 14 days reached a constant equilibrium concentration of 40 - 60  $\mu\text{g}/\text{m}^3$ .

15 The samples according to the invention permit to obtain a clear decrease of the concentration from 220  $\mu\text{g}/\text{m}^3$  to a final concentration of 40-60  $\mu\text{g}/\text{m}^3$  which is well below the legal limit value of 120  $\mu\text{g}/\text{m}^3$ .

**Example 2: Determination of the catalytic benzene degradation property of the carpets according to the invention under continuous aeration.**

For the study of the effect of the carpet of the invention on the benzene degradation a  
20 concentration of 45  $\mu\text{g}/\text{m}^3$  +/- 15  $\mu\text{g}/\text{m}^3$  was applied in the test chamber by means of a continuous air supply over a Teflon hose at an air exchange rate of 0.5/h. The test chambers were operated at a temperature of 20°C and a relative humidity of 50 %.

The benzene originates from a 50 NI content high-grade steel container containing a  
25 concentrated benzene atmosphere of 11200  $\mu\text{g}/\text{m}^3$ , in constant equilibrium between liquid and gaseous state at 20 °C and 50 % relative humidity. The benzene flows out of this container at an air flow of 3.0 l/h (50 ml/min) and is mixed with pure air in ratio of 1:26. The air flows out of the test chambers at a flow rate of 180 l/h, wherein 24.8 l were sampled by means of diaphragm pumps.

The measurement of the benzene concentrations were performed at the times t = 0, 2, 8  
30 and 24 hours and after 2, 4, 7 and 14 days, so that altogether 8 samplings were performed by means of direct withdrawal from Septen with syringes.

In the test chamber without samples the appropriate measurements were made likewise at 0, 8, 24 hours as well as 7 and 14 days .

The laboratory tests were performed according to the respective DIN procedures and/or regulations wherein the benzene concentration was measured by use of the Tenax absorbent. Subsequently, the samples were examined by gas chromatography with the GG/FID/ECD.

5 The results of this experiment are shown in Figure 3 for the coated samples, as well as the uncoated sample and the control measurement without sample.

It can be seen from Figure 3 that after only few hours a clear decrease in the benzene concentration was observed when using the carpet samples according to the invention. Indeed the concentration decreased from 45 µg/m<sup>3</sup> to 10 µg/m<sup>3</sup> which is the detection limit

10 for benzene.

**Example 3: Olfactory evaluation of tobacco odor deodorant property of the carpets according to the invention**

For this experiment cigarette smoke -corresponding to the content of a room wherein 50 cigarettes are consumed daily- was applied in the test chamber by means of a continuous 15 air supply over a Teflon hose at an air exchange rate of 0.5/h. The test chambers were operated at a temperature of 20°C and a relative humidity of 50 %.

The cigarette smoke originates from a 50 NI content high-grade steel container containing a concentrated cigarette smoke atmosphere at 20 °C and 50 % relative humidity. The cigarette smoke flows out of this container at an air flow of 5.2 l/h (87 ml/min) and is mixed 20 with pure air in ratio of 1:3.6 so as to obtain in the test chamber a concentration equivalent to the smoke of 50 cigarettes consumed daily.

The air flows out of the test chambers and 24.8 l were sampled by means of diaphragm pumps. The odor evaluation was performed for samples according to the invention as well as for controls not containing TiO<sub>2</sub> at the times t = 0, 2, 8 and 24 hours and after 2, 4, 7 25 and 14 days, so that altogether 8 samplings were performed by means of direct withdrawal from Septen with syringes.

Additionally a control measurement was performed in a test chamber without sample likewise at 0, 8, 24 hours as well as 7 and 14 days.

The olfactometry measurements were performed according to the respective VDI 30 recommendation 3881, Sheet I and II, whereby the odor intensity (GI with a scaling from 0 to 5 corresponding to 5: intense odor, 4: strong odor, 3: readily perceptible, 2: weak odor perceptible, 1: barely perceptible odor, 0: no odor) and the odor development/ Hedonik

(GA with a scaling from -5 to +5 ) were evaluated. Three independent test persons made the respective odor evaluation and means values were calculated.

The results of this experiment are shown in Figures 4 and 5. It can be seen from figures 4 and 5 that after few hours the intensity of the smoke odor decreased drastically for all the 5 samples according to the invention when compared with the controls.

**Example 4 Determination of the catalytic TVOC degradation property of the carpets according to the invention under continuous aeration.**

In addition to the olfactory evaluation of tobacco odor deodorant property of the carpets according to the invention the effect of the catalytic activity of the carpets according to the 10 invention on the total content of volatile organic compound was also measured

Similarly to example 3, for this experiment cigarette smoke -corresponding to the content of a room wherein 50 cigarettes are consumed daily- was applied in the test chambers by means of a continuous air supply over a Teflon hose at an air exchange rate of 0.5/h. The test chambers were operated at a temperature of 20°C and a relative humidity of 50 %.

15 The cigarette smoke originates from a 50 NI content high-grade steel container containing a concentrated cigarette smoke atmosphere at 20 °C and 50 % relative humidity. The cigarette smoke flows out of this container at an air flow of 5.2 l/h (87 ml/min) and is mixed with pure air in ratio of 1:3.6 so as to obtain in the test chamber a concentration equivalent to the smoke of 50 cigarettes consumed daily.

20 The air flowed out of the test chambers and 24.8 l were sampled by means of diaphragm pumps. The evaluation of the TVOC content was performed for coated and uncoated carpet at the times  $t = 0, 2, 8$  and 24 hours and after 2, 4, 7 and 14 days, so that altogether 8 measurements were performed by means of GC/PID. Additionally a control measurement was performed in a test chamber without sample likewise at 0, 8, 24 hours 25 as well as 7 and 14 days.

The determination of the total content of volatile organic compounds (TVOC content) was performed by a portable gas chromatograph PE Photovac Voyager. In order to obtain representative values, 5 measurements were performed every 10 min. Calibration of the chromatograph was performed using a defined toluol standard. The detection used a 30 photoionization detector with quick-change electrodeless discharge UV lamp, 10.6 eV.

The results of this experiment are shown in Figure 6, wherein it can be seen that the sample according to the invention provided a TVOC degradation in the order of 60-70%.

**Example 5 Determination of the catalytic formaldehyde degradation property of the carpets according to the invention under continuous aeration: Influence of the UV Irradiation duration**

In this example, the influence of the UV light on the catalytic formaldehyde degradation 5 property of the carpets according to the invention was investigated. The catalytic degradation property was measured by the analysis of the effect of the coated carpets on formaldehyde degradation under different UV light expositions.

The carpet samples were made from 40 cm x 40 cm carpet pieces. From these carpet 10 pieces, carpet samples of 7.8 cm x 7.8 cm were manufactured and masked by means of an aluminum tape in order to avoid edge effects during the measurement of the catalytic degradation of the formaldehyde. Formaldehyde degradation was investigated under continuous aeration by chamber testing and compared with uncoated carpet samples, and with a control without sample.

The test chambers are airtight aluminum boxes which have a volume of 49.58 l, the 15 proportion between the tested sample and the chamber volume amounts to 1.23 m<sup>2</sup>/m<sup>3</sup> in a standard inspection surface of 61 cm<sup>2</sup>. The carpet samples were placed in the center of the test chambers and locked therein. A UV lamp 3 mW/cm<sup>2</sup> was fixed in the chamber on the top.

The experiment was set up in accordance with the usual daily light intensities which can 20 be expected during the different seasons and weather conditions. The experiment started by simulating winter conditions consisting of 10-hour light exposure under cloudy conditions which is estimated at 0.15 W/cm<sup>2</sup> for 10 hours, with half-hour irradiation of 3 mW/cm<sup>2</sup>. The experiment carried on by extending the daily irradiating duration by 1, 2, 4, 25 6 and 8 hours, in order to simulate irradiation expected during the transition periods of spring and autumn as well as maximum exposure in the summer time area. The results were compared to those obtained using uncoated carpet samples or control measurements without samples.

A defined formaldehyde concentration of 220 µg/m<sup>3</sup> +/- 30 µg/m<sup>3</sup> (which corresponds to the average formaldehyde content in a smoker room) was applied in the test chamber by 30 means of a continuous air supply over a Teflon hose at an air exchange rate of 0.5/h. The test chambers were operated at a temperature of 20°C and a relative humidity of 50 %.

The formaldehyde originates from a 50 Ni content high-grade steel container containing a concentrated formaldehyde atmosphere of 54000 µg/m<sup>3</sup>, in constant equilibrium between liquid and gaseous state at 20 °C and 50 % relative humidity. The formaldehyde flows out

of this container at an air flow of 3.0 l/h (50 ml/min) and is mixed with pure air in ratio of 1:245. The air flows out of the test chambers at a flow rate of 130 l/h, wherein 24.8 l were sampled by means of diaphragm pumps.

5 The measurement of the formaldehyde concentrations were performed at the times t = 0, 2, 8 and 24 hours and after 2, 4, 7 and 14 days, so that altogether 8 samplings were performed by means of direct withdrawal from Septen with syringes. In an additional control chamber without sample the appropriate measurements were made likewise at 0, 8, 24 hours as well as 7 and 14 days.

10 The laboratory tests were performed according to the respective DIN procedures and/or regulations wherein the aldehyde concentration was measured by use of the DNPH method (dinitrophenylhydrazine = DNPH). Subsequently, the samples were examined photometrically using pararosanilin procedure on formaldehyde.

15 The results of this experiment are shown in Figure 7. It can be seen from figure 7 that after few hours a clear decrease in the formaldehyde concentration was observed for the coated carpet samples wherein the concentration after 14 days reached a constant equilibrium concentration of 40 - 60  $\mu\text{g}/\text{m}^3$  independently of the UV light irradiation duration.

20 This experiment shows that winter light conditions even under cloudy weather are sufficient to induce a catalytic degradation of formaldehyde content of a room by the coated carpet according to the invention.

25 A very effective decrease in formaldehyde concentration is obtained in the course of the experiment with all the UV intensities tested, wherein a final concentration of 50-60  $\mu\text{g}/\text{m}^3$  is attained which is well below the legal limit value of 120  $\mu\text{g}/\text{m}^3$ . The carpets according to the invention are therefore very effective in cleaning air and removing harmful compounds from the air.

**Example 6 Determination of the air cleaning durability of a carpet according to the invention under conditions intended to simulate a 5 year cycle of maintenance.**

30 In this example, the air cleaning durability of a carpet according to the invention was evaluated under conditions intended to simulate a 5 year cycle of maintenance. The catalytic formaldehyde degradation properties of the carpets according to the invention which have been vacuum cleaned and/or 1 time laundered, was investigated by chamber testing and compared with untreated samples.

The carpet samples were made from 200 cm x 100 cm carpet pieces which were vacuum

cleaned. For this experiment, in order to simulate a 5 year cycle of maintenance wear, the carpet pieces were vacuumed 500 times each with a back and forth motion using a usual household-vacuum cleaner of 1200 Watt. This treatment corresponds to a usual regular cycle 2 times weekly carpet care over 5 years. Subsequently, a laundering took place at 5 30 °C with the addition of a commercial carpet preservative agent.

After vacuum cleaning and washing, carpet samples of 7.8 cm x 7.8 cm were manufactured and masked by means of an aluminum tape in order to avoid edge effects during the measurement of the catalytic degradation of the formaldehyde.

The test chambers are airtight aluminum boxes which have a volume of 49.58 l, the 10 proportion between the tested sample and the chamber volume amounts to 1.23 m<sup>2</sup>/m<sup>3</sup> in a standard inspection surface of 61 cm<sup>2</sup>. The carpet samples were placed in the center of the test chambers and locked therein. A UV lamp 3 mW/cm<sup>2</sup> was fixed in the chamber on the top. The samples were incubated over a period of 14 days with constant irradiation by a UV lamp with a radiation intensity of 3 mW/cm<sup>2</sup>. As a control sample, a carpet according 15 to the invention which had not been vacuumed was used.

A defined formaldehyde concentration of 220 µg/m<sup>3</sup> +/- 30 µg/m<sup>3</sup> was applied in the test chamber by means of a continuous air supply over a Teflon hose at an air exchange rate of 0.5/h. The test chambers were operated at a temperature of 20°C and a relative humidity of 50 %.

20 The formaldehyde originates from a 50 NI content high-grade steel container containing a concentrated formaldehyde atmosphere of 54000 µg/m<sup>3</sup>, in constant equilibrium between liquid and gaseous state at 20 °C and 50 % relative humidity. The formaldehyde flows out of this container at an air flow of 3.0 l/h (50 ml/min) and is mixed with pure air in ratio of 1:245. The air flows out of the test chambers at a flow rate of 180 l/h, wherein 24.8 l are 25 sampled by means of diaphragm pumps.

The measurement of the formaldehyde concentrations were performed at the times t = 0, 2, 8 and 24 hours and after 2, 4, 7 and 14 days, so that altogether 8 samplings were performed by means of direct withdrawal from Septen with syringes.

30 Appropriate measurements were made likewise in an additional control chamber without sample at 0, 8, 24 hours as well as 7 and 14 days.

The laboratory tests were performed according to the respective DIN procedures and/or regulations wherein the aldehyde concentration was measured by use of the DNPH method (dinitrophenylhydrazine = DNPH). Subsequently, the samples were examined photometrically using pararosanilin procedure on formaldehyde.

The results of this experiment are shown in Figure 8, for each of the samples: vacuum cleaned sample, washed sample, untreated sample and control without sample. The results show no negative effects after vacuum cleaning and 1 washing. It can be seen in Figure 8 that a 5 year maintenance cycle does not have any effect on the formaldehyde degradation properties of the carpets according to the invention. Regular vacuuming and washing of the carpets of the invention does not alter the air cleaning efficacy of said carpet. With all the tested samples a decrease in the formaldehyde concentration was observed from 220 µg/m<sup>3</sup> to well below the legal value of 120 µg/m<sup>3</sup> for formaldehyde.

**Example 7 Determination of the catalytic formaldehyde degradation property of the laminates according to the invention**

In this example, the catalytic activity of the laminates according to the invention was measured by the analysis of the formaldehyde degradation under continuous aeration. sample 0 (without titanium dioxide), sample 1 (with 0.076 % titanium dioxide) and sample 2 (with 1 % titanium dioxide).

15 The laminates used in this experiment consisted of 30 cm x 10 cm laminates. From these laminates, samples of 7.8 cm x 7.8 cm were manufactured and masked by means of an aluminum tape in order to avoid edge effects during the measurement of the catalytic degradation of formaldehyde. Formaldehyde degradation was investigated under continuous aeration by chamber testing and compared control samples.

20 The test chambers are airtight aluminum boxes which have a volume of 49.58 l, the proportion between the tested sample and the chamber volume amounts to 1.23 m<sup>2</sup>/m<sup>3</sup> in a standard inspection surface of 61 cm<sup>2</sup>. The carpet samples were placed in the center of the test chambers and locked therein. A UV lamp 3 mW/cm<sup>2</sup> was fixed in the chamber on the top.

25 A defined formaldehyde concentration of 220 µg/m<sup>3</sup> +/- 30 µg/m<sup>3</sup> (which corresponds to the average formaldehyde content in a smoker room) was applied in the test chamber by means of a continuous air supply over a Teflon hose at an air exchange rate of 0.5/h. The test chambers were operated at a temperature of 20°C and a relative humidity of 50 %.

30 The formaldehyde originates from a 50 NI content high-grade steel container containing a concentrated formaldehyde atmosphere of 54.000 µg/m<sup>3</sup>, in constant equilibrium between liquid and gaseous state at 20 °C and 50 % relative humidity. The formaldehyde flows out of this container at an air flow of 3.0 l/h (50 ml/min) and is mixed with pure air in ratio of 1:245. The air flows out of the test chambers at a flow rate of 180 l/h, wherein 24.8 l were sampled by means of diaphragm pumps.

The measurement of the formaldehyde concentrations were performed at the times  $t = 0$ , 2, 8 and 24 hours and after 2, 4, 7 and 14 days, so that altogether 8 samplings were performed by means of direct withdrawal from Septen with syringes. Appropriate measurements in an additional control chamber without sample were made likewise at 0, 5 8, 24 hours as well as 7 and 14 days.

The laboratory tests were performed according to the respective DIN procedures and/or regulations wherein the aldehyde concentration was measured by use of the DNPH method (dinitrophenylhydrazine = DNPH). Subsequently, the samples were examined photometrically using pararosanilin procedure on formaldehyde.

10 The results of this experiment are shown in Figure 9. It can be seen from figure 9 that after few hours a clear decrease in the formaldehyde concentration was observed for the laminate samples according to the invention wherein the concentration after 14 days reached a constant equilibrium concentration of 80 - 130  $\mu\text{g}/\text{m}^3$ .

15 The formaldehyde-level decreases in the indoor air significantly with higher concentration of  $\text{TiO}_2$  in the highest layer of the laminate

**Example 8: Determination of the catalytic benzene degradation property of the laminates according to the invention**

For the study of the effect of the laminate of the invention on the benzene degradation a concentration of  $45 \mu\text{g}/\text{m}^3 \pm 15 \mu\text{g}/\text{m}^3$  was applied in the test chamber by means of a 20 continuous air supply over a Teflon hose at an air exchange rate of 0.5/h. The test chambers were operated at a temperature of  $20^\circ\text{C}$  and a relative humidity of 50 %.

The benzene originates from a 50 NI content high-grade steel container containing a 25 concentrated benzene atmosphere of  $11200 \mu\text{g}/\text{m}^3$ , in constant equilibrium between liquid and gaseous state at  $20^\circ\text{C}$  and 50 % relative humidity. The benzene flows out of this container at an air flow of 3.0 l/h (50 ml/min) and is mixed with pure air in ratio of 1:26. The air flows out of the test chambers at a flow rate of 180 l/h, wherein 24.8 l were sampled by means of diaphragm pumps.

The measurement of the benzene concentrations were performed at the times  $t = 0, 2, 8$  and 24 hours and after 2, 4, 7 and 14 days, so that altogether 8 samplings were 30 performed by means of direct withdrawal from Septen with syringes.

In the test chamber without samples the appropriate measurements were made likewise at 0, 8, 24 hours as well as 7 and 14 days.

The laboratory tests were performed according to the respective DIN procedures and/or

regulations wherein the benzene concentration was measured by use of the Tenax absorbent. Subsequently, the samples were examined by gas chromatography with the GG/FID/ECD.

5 The results of this experiment are shown in Figure 10. It can be seen from figure 10 that after few hours a clear decrease in the benzene concentration was observed when using the laminate according to the invention compared to the control laminate.